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INVESTIGATION OF THE STRUCTURE OF Si_3N_4-BASED CERAMIC WITH Al_2O_3 AND Y_2O_3 ADDITIVES

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A ceramic with dense nanosize structure was obtained by conventional sintering of samples formed from nanosize Si_3N_4 powder with Al_2O_3 and Y_2O_3 additives by cold isostatic pressing. The microstructure and density of the ceramic obtained were investigated. The technological conditions for obtaining silicon nitride ceramic that give the optimal combination of fine-grain submicron structure and high density were determined.

Key words: ceramic, silicon nitride, cold isostatic pressing, nanostructure, composite.

The promising ceramic materials based on silicon nitride are characterized by a wide range of applications, which is a result of the extremely good combination of properties and characteristics of this material. In particular, silicon nitride ceramic differs beneficially from other types of ceramic by high strength, heat resistance, radio transparency, thermal conductivity, low linear thermal expansion coefficient (CLTE) and resistance to abrasive wear. Si_3N_4-based ceramic is widely used in the aerospace industry, in engines, nuclear and chemical industries and metallurgy [1].

The diversity of methods of synthesis and consolidation of silicon-nitride powders is described in detail in the domestic literature [5]. The particulars of this type of ceramic are investigated in detail in [2]. A number of methods of pressing are also known: cold static pressing (CSP), hot isostatic pressing (HIP) [9] and others. However, the authors of [3] posit that simple sintering is the most expedient way to reach the goal stated. The process of making a compression mold is of no small importance and labor-intensive; silicone compression molds are considered to be preferable [6].

The properties of powders, such as structuring and the sizes and shapes of particles and aggregates, play a fundamental role in the sintering process in ceramics. As an example, the authors of [4] note that the size of the initial particles of the α-phase of the powder affects the rate of the α–β phase transition and the evolution of the structure of ceramic material during the sintering process. It was determined that the preferred powder is one with fine-size initial components. Addition heat treatment is used effectively to increase the thermal and mechanical characteristics after sintering [7]. In addition, additional additives, such as rare-earth metal oxides, are often added into the batch [9]. The particulars of the microstructure of ceramic based on silicon nitride with the addition of yttrium oxide are presented in [7].

Our aim in the present work is to obtain ceramic with the composition $Si_3N_4 + Al_2O_3 + Y_2O_3$ by conventional sintering of samples obtained by cold isostatic pressing.

EQUIPMENT AND EXPERIMENTAL PROCEDURE

The standard ceramic technology, which includes batch preparation, pressing, sintering and final machining, was used to obtain high-density ceramic.

Stark, Grade M11 (particle size 600 nm) silicon nitride Si_3N_4 (85%), produced in Germany by the conventional technology, was used as the initial material. In addition, Y_2O_3 powder (Stark, Grade, 2 μm) and nanosize Al_2O_3 (A16 SG, 600 nm) were introduced into the batch. The content of oxide additives was 15 wt.%. The powders were mixed in a Retsch RS-200 disk mill. The preparation time of the mixtures was 20 min. The mixing rate was 250 min^{-1}.

The method of cold isostatic pressing (CIP) was chosen to make the samples. The batch obtained was loaded into elastic compression molds and an EPSI CIP 400 B-9140 press was used to compact the samples at room temperature and pressure 200 MPa. The sintering process was conducted in a nitrogen atmosphere in a Nabertherm VHT 8/22-GR high-temperature furnace. The sintering temperature in the

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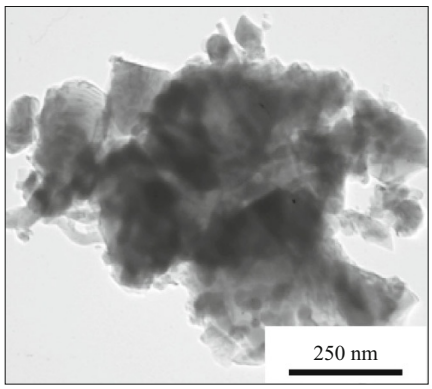

Fig. 1. TEM image of an agglomerate of Si_3N_4 powder.

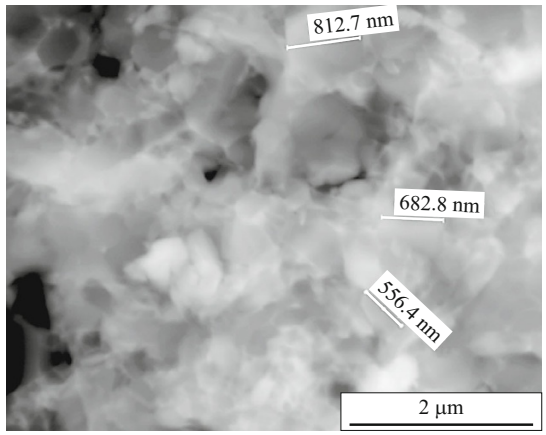

Fig. 2. SEM image of the structure of sintered silicon-nitride-based ceramic at 1600°C (soaking time 1 h).

range 1500 – 1700°C was determined experimentally; the soaking time was 1 h.

A Quanta 600 scanning electron microscope (SEM) equipped with an attachment, manufactured by the EDAX Company, for performing energy-dispersion analysis was used to investigate the microstructure. The investigation was performed on chip surfaces of the experimental samples.

A JEM-2100 transmission electron microscope with accelerating voltage 200 kV, equipped with an attachment for performing local chemical analysis, was used to observe the fine structure. The samples for investigating the structure by means of transmission electron microscopy were prepared by mechanical polishing on abrasive grinding paper with grain size reduced at the subsequent polishing using an OP-S polishing suspension.

Samples in the form of thin foil were prepared from a polished sample by ionic etching. These foils were placed in an Ion Milling Model 1010 ion gun, manufacture by the Fischione Company, for final polishing of the foil by the ion gun (voltage 5 kV, current 5 mA). Before an opening was formed the initial angle of polishing was 11°. Next, the sample was positioned at the angle 9° (for 20 min).

The pycnometric density of the sintered ceramic samples was determined by helium pycnometry (AccuPyc II 1340).

RESULTS AND DISCUSSION

The porosity of the article must be low in order to obtain a strong ceramic. It is logical to expect that a high-porosity ceramic is characterized by low strength because the contact area of the grains and the stress concentration in the weakened sections decrease. For this reason, needle particle morphology is undesirable for the initial powders in this case. Thus, it is obvious that another basic factor imparting high strength to ceramic materials is the specific structural nature of the particles of the initial powders. Analysis of the particle shape and size in the initial powders performed with a transmission electron microscope (TEM) showed that the Si_3N_4 powder obtained after calcination in a furnace is comprised of conglomerates with average size 1 μm (Fig. 1), themselves consisting of smaller (30 – 100 nm) crystallites possessing irregular shapes with faceting.

The powder oxide additives Y_2O_3 (particle size 2 μm) and nanosize Al_2O_3 (particle size 600 nm) were introduced in the batch preparation process in order to densify the compact during the decomposition of Si_3N_4 (Si_3N_4 decomposes at 1450°C) owing to high-temperature synthesis of the new phases — the compounds $Si_{6-z}Al_zO_zN_8$ and $Y_3Al_5O_{12}$. The composition of the batch is (wt.%): Si_3N_4 — 85, Al_2O_3 — 6 and Y_2O_3 — 9.

SEM images of the structure of the silicon nitride based ceramic sintered at 1600°C with 1 h soaking are presented in Fig. 2. The presence of a dense submicron structure is clearly seen. The average size of the structural components varies in the range 100 – 800 nm.

It was determined experimentally that 1600°C is the optimal sintering temperature for obtaining samples with the maximum density. In the course of this work the fine structure of the ceramic obtained was investigated. A close-packed structure with clear-cut intergrain boundaries was revealed. The average grain size is 200 nm.

The pycnometric density of the Si_3N_4-based ceramic obtained was 3.1 g/cm^3. The theoretical density of Si_3N_4 is 3.4 g/cm^3.

The data obtained attest that the pycnometric density of the experimental samples is higher than 90% of the theoretical density of silicon nitride, which is high.

CONCLUSIONS

Analysis of the results obtained shows that the powder composition $Si_3N_4 + Al_2O_3 + Y_2O_3$, based on the nanodisperse powders Si_3N_4 and Al_2O_3, makes it possible to obtain a high-density ceramic with a fine-grain equiaxial structure with grain size 200 nm. The pycnometric density of the ceramic obtained is greater than 90% of the theoretical density of Si_3N_4.

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